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# Ab initio quantum chemical study of electron transfer in carboranes

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## Abstract

The electron transfer (ET) properties of 10- and 12-vertex carboranes are investigated by the ab initio Hartree–Fock method within the Marcus–Hush (MH) *two-state* model and the Koopman theorem (KT) approach. The calculated value of the ET coupling matrix element,  $V_{AB}$ , is consistently higher in the KT approach than in the MH *two-state* model. For the carborane molecules functionalized by  $-\text{CH}_2$  groups at C-vertices,  $V_{AB}$  strongly depends on the relative orientation of the planes containing the terminal  $-\text{CH}_2$  groups. The predicted conformation dependence of  $V_{AB}$  offers a molecular mechanism to control ET between two active centers in molecular systems.

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## 1. Introduction

Carboranes are an important class of boron-containing rigid structures that have potential applications in medicinal drug design as hydrophobic pharmacophores [1], as antisense agents for antisense oligonucleotide therapy (AOT) [2], as boron carriers for boron neutron capture therapy (BNCT) [3–5], and as molecular probes for molecular medical diagnostics [6], among others. Recently, heteroisomeric diodes, based upon the chemical vapor deposition of different isomers of *closo*-dicarbado-dodecaborane, namely *closo*-1,2-dicarbado-dodecaborane (orthocarborane,  $\text{C}_2\text{B}_{10}\text{H}_{12}$ ) and *closo*-1,7-dicarbado-dodecaborane (metacarborane,  $\text{C}_2\text{B}_{10}\text{H}_{12}$ ), which have important applications as solid state neutron detectors have also been fabricated [7]. Due to their axially directed terminal bonds and rigid cage structures, carboranes

also offer a unique opportunity in the area of molecular engineering for their potential application as a molecular anchor between two active reaction centers, and have been the subject of numerous experimental and theoretical studies [8–11]. It has been found that electron transfer (ET) across the carborane cage plays an important role in controlling the redox process in Ni-carboranes [12]. Therefore, an understanding of the electron transfer process across the carborane cages and its relationships to molecular geometry and electronic structure is deemed important. Such an understanding is also crucial for the future application of carboranes in molecular-scale electronics. It has recently been predicted [13–16] that  $\sigma$ -bonded carbon cage structures can be used as an effective electron tunnel barrier in molecular-scale electronic circuits.

In this Letter, we present ab initio investigations of the electronic structure and ET coupling strengths in *closo*-1,10-dicarbado-dodecaborane ( $\text{C}_2\text{B}_8\text{H}_{10}$ ), and *closo*-1,12-dicarbado-dodecaborane ( $\text{C}_2\text{B}_{10}\text{H}_{12}$ ) and their  $-\text{CH}_2$  derivatives, namely, 1,10-dimethylene-1,10-dicarba-*closo*-

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decaborane ( $\text{H}_2\text{C}-\text{CB}_8\text{H}_8\text{C}-\text{CH}_2$ ), and 1,12-dimethylene-1,12-dicarba-*closo*-dodecaborane ( $\text{H}_2\text{C}-\text{CB}_{10}\text{H}_{10}\text{C}-\text{CH}_2$ ). These carborane molecules will be referred to in the rest of this Letter as 10-vertex and 12-vertex carborane molecules, respectively. The ET coupling strength is calculated using the MH *two-state* model [17–21] within ab initio Hartree–Fock theory. The effects of basis sets and geometrical parameters on the ET coupling strength are also investigated. For comparison, the ET coupling strength is also estimated using the KT approach [17].

In Section 2, the computational approach employed in the present study is briefly described. The results and discussions follow in Section 3. The main findings of the present study are summarized in Section 4.

## 2. Computational approach

Ab initio Hartree–Fock (HF) and density functional theory (DFT) calculations of equilibrium geometry and electronic structure were performed with the GAUSSIAN quantum chemistry program package [22]. The geometrical parameters were obtained with the use of a minimal basis set (STO-3G) as well as an extended basis set consisting of a double zeta augmented by one *p* and one *d* polarization functions (DZP) as implemented in the Gaussian [22] basis set library. The extended basis set is referred to as the DZP basis set in the remainder of the Letter. In the DFT calculations, the B3LYP [23] exchange–correlation functional was employed.

The electron transfer coupling strength,  $V_{\text{AB}}$ , is calculated using the MH *two-state* (TS) model the details of which can be found in various review articles [17–21]. Briefly, the ET rate constant for a weak coupling (i.e., non-adiabatic limit) between electron donor and acceptor centers can be obtained from the Fermi Golden rule as [17]

$$K_{\text{et}} = \frac{2\pi}{\hbar} |V_{\text{AB}}|^2 \text{FCWD}, \quad (1)$$

where FCWD represents a Franck–Condon-weighted density of states, which reflects the nuclear modes of the system. The ET coupling matrix element,  $V_{\text{AB}}$ , which plays a major role in the ET process, represents the strength of the interaction between the two active reaction sites, and is given by [21]

$$V_{\text{AB}} = (1 - S_{\text{AB}}^2)^{-1} [H_{\text{AB}} - S_{\text{AB}}(H_{\text{AA}} + H_{\text{BB}})/2], \quad (2)$$

where

$$H_{\text{AB}} = \langle \Psi_{\text{A}} | H | \Psi_{\text{B}} \rangle, \quad (3)$$

$$H_{\text{AA}} = \langle \Psi_{\text{A}} | H | \Psi_{\text{A}} \rangle, \quad (4)$$

$$H_{\text{BB}} = \langle \Psi_{\text{B}} | H | \Psi_{\text{B}} \rangle, \quad (5)$$

and

$$S_{\text{AB}} = \langle \Psi_{\text{A}} | \Psi_{\text{B}} \rangle. \quad (6)$$

Here,  $S_{\text{AB}}$  is the overlap matrix element.  $H$  is the electronic Hamiltonian of the system, and  $\Psi_{\text{A}}$  and  $\Psi_{\text{B}}$  are the localized many-electron wave-functions of the two states A and B, respectively.

In the present study, the ab initio unrestricted Hartree–Fock (UHF) method was used to generate the localized states of the molecules. These localized wave-functions were subsequently used as the initial guess in the self-consistent evaluation of the ET coupling matrix element. The nuclear configuration used for the calculation of the ET matrix element was taken to be the geometric average of the two localized structures, where  $H_{\text{AA}} = H_{\text{BB}}$ . It is important to note that Eq. (2) assumes the validity of the Condon approximation (i.e.,  $V_{\text{AB}}$  is a weak function of the nuclear coordinates) in the vicinity of the transition state [17].

For the parent 10- and 12-vertex carboranes (i.e.,  $\text{C}_2\text{B}_8\text{H}_{10}$  and  $\text{C}_2\text{B}_{10}\text{H}_{12}$ ), a symmetry-constrained optimization was performed to obtain the respective equilibrium structures. A model  $\pi$ -cage- $\pi$  structure containing two active reaction centers was then constructed by replacing the terminal H atoms by  $-\text{CH}_2$  groups yielding a *two-state* system. The resulting structures of the derivative carboranes are shown in Fig. 1 where the  $-\text{CH}_2$  groups are the active reaction centers. The derivative molecules were then optimized in the singly positively charged doublet state. A pair of equilibrium structures, which by convention we term as left-localized and right-localized structures, were obtained by varying the C–C bond distance between the cage and each of the  $-\text{CH}_2$  end groups, keeping the cage structure fixed.

The localized wavefunctions obtained for the derivative carboranes (i.e.,  $[\text{C}_4\text{B}_8\text{H}_{12}]^+$  and (i.e.,  $[\text{C}_4\text{B}_{10}\text{H}_{14}]^+$ ) were used as the initial guess for the calculation of the ET coupling element at the average of the left-localized and right-localized asymmetric configurations. In order to examine the effects of nuclear configurations on  $V_{\text{AB}}$ , *two-state* model calculations were also performed at one of the localized geometries, namely the left-localized asymmetric configuration. Calculations of  $V_{\text{AB}}$  in the *two-state* model were performed with the HONDO-8 electronic structure suite [24].

The  $V_{\text{AB}}$  of a singly-charged positive ion can also be calculated within the KT approach as [17]

$$V_{\text{AB}} = 1/2(\varepsilon_{\text{HOMO}} - \varepsilon_{\text{HOMO}-1}), \quad (7)$$

where  $\varepsilon_{\text{HOMO}}$  and  $\varepsilon_{\text{HOMO}-1}$  are energies of the highest occupied molecular orbital (HOMO) and the next highest occupied molecular orbital in the triplet state of the neutral molecule. The HOMO and HOMO-1 orbitals correspond to the symmetric and anti-symmetric combination of the p-orbitals of the terminal end groups, respectively. The KT approach has been successfully

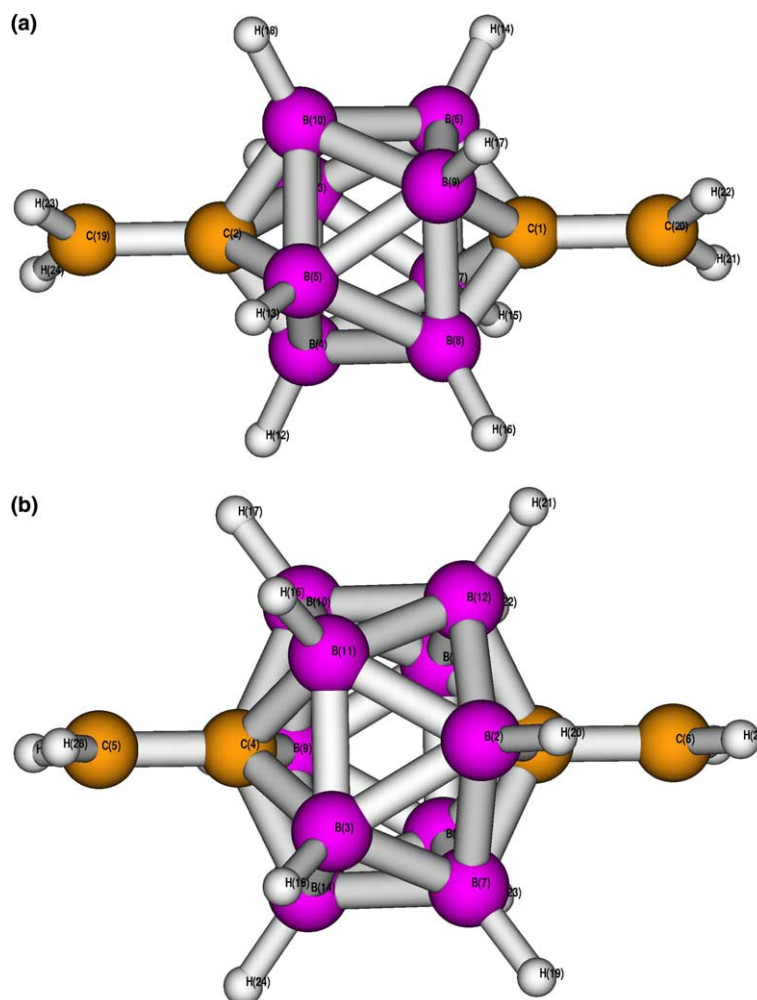


Fig. 1. The equilibrium structures of (a) 10- and (b) 12-vertex carborane molecules obtained using the ab initio Hartree–Fock method.

used to study ET properties of a wide range of organic structures [25–28] and generally yields  $V_{AB}$  values comparable to more rigorous methods [29]. However, it was noted in a previous study [13] that the magnitude of  $V_{AB}$  obtained in the KT approach is generally larger than that obtained using the MH *two-state* approach at a similar level of theory.

### 3. Results and discussion

#### 3.1. Geometry

The equilibrium structural parameters, in this case the bond lengths of the cage portions, of the parent 10- and 12-vertex carboranes ( $C_2B_8H_{10}$  and  $C_2B_{10}H_{12}$ ) shown in Fig. 1 are presented in Table 1. One notes that the optimized geometrical parameters are relatively insensitive to the choice of the basis set. The HF and DFT(B3LYP) methods are also in good accord with each other. While there are no experimental reports on

the geometrical parameters for  $C_2B_8H_{10}$  and  $C_2B_{10}H_{12}$ , the structural parameters for similar systems,  $B_{10}H_{10}^{2-}$  and  $B_{12}H_{12}^{2-}$ , have been reported [30,31]. For the bond length between a pair of B atoms generated by single 4- and 5-fold proper rotations, such as the bonds between B(8)–B(9) in Fig. 1a and B(3)–B(11) in Fig. 1b, the reported values are 1.88 and 1.77 Å for the 10- and

Table 1  
Calculated lengths of typical bonds in 10- and 12-vertex carboranes

Molecule	Bond length (Å)	HF (STO-3G)	HF (DZP)	DFT-B3LYP (DZP)
$C_2B_8H_{10}$	C(1)–B(8)	1.603	1.601	1.607
	B(8)–B(9)	1.869	1.869	1.869
	B(5)–B(9)	1.829	1.834	1.825
$C_2B_{10}H_{12}$	C(4)–B(3)	1.710	1.710	1.711
	B(3)–B(11)	1.789	1.797	1.797
	B(2)–B(3)	1.760	1.780	1.780

The labeling of the atoms is shown in Fig. 1.

12-vertex boranes, respectively. These values are in good agreement with the calculated HF (DZP) values of 1.87 and 1.80 Å in the corresponding carboranes. The bond length between a pair of B atoms related by a single 8-fold improper rotation in the 10-vertex carborane, such as the bonds between B(5)–B(9) in Fig. 1a and B(2)–B(3) in Fig. 1b, has been reported [30] to be 1.82 Å, which is close to the corresponding bond distance (1.84 Å) obtained in our ab initio HF (DZP) calculation.

In the degenerate ionized configurations (i.e., left-localized and right-localized asymmetric configurations) of the derived 10- and 12-vertex carboranes, the C(CH<sub>2</sub>)–C(cage) bond length is found to be shorter, by approximately 0.06 Å, on the side of the cage on which the single positive charge is localized. For example, the respective values of  $R_{(C1-C20)}$  and  $R_{(C2-C19)}$  are 1.41 and 1.47 Å in the 10-vertex carborane molecule at the HF(DZP) level of theory. Similarly, the HF(DZP) values of  $R_{(C1-C6)}$  and  $R_{(C4-C5)}$  are 1.43 and 1.49 Å, respectively, in the 12-vertex carborane molecule.

### 3.2. Computation of the ET matrix element

The values of  $V_{AB}$  calculated in the MH model with the use of the minimal and the extended basis sets are presented in Table 2. In the calculations, the –CH<sub>2</sub> end groups of the carborane molecules were kept co-planar. It is clear from the table that the choice of the basis set has a small but noticeable effect on the calculated value of  $V_{AB}$ . The DZP basis set used in the study yields ~10% larger value for  $V_{AB}$  than the STO-3G basis set. However, negligible, if any, difference is noted in the value of  $V_{AB}$  between the localized (i.e.,  $H_{AA} \neq H_{BB}$ ) and the average (i.e.,  $H_{AA} = H_{BB}$ ) structure, justifying the validity of Condon approximation [17,18] used in deriving Eq. (2).

The values of  $V_{AB}$  estimated using the KT approach Eq. (7) from the one-electron energy levels are 70.9 and 64.7 kJ/mol for the 10-vertex and 12-vertex carboranes, respectively. These values are ~36% and 38% larger than the corresponding values obtained from the MH *two-state* approach (Table 2) at the same level (i.e.,

HF approach with DZP basis set) of theory. Similar differences in the calculated values of  $V_{AB}$  in the KT and MH approaches were noted in our previous study [13,14] on carbon cage structures.

Between the 10-vertex and 12-vertex carboranes, a decrease in the ET coupling with an increase in cage size is observed. This is consistent with our previously reported results [13] for carbon-based spacers. We also note here that the ET coupling matrix element for the 10-vertex carborane is nearly the same as that for the smaller carbon-based cage structured bicyclo[1.1.1]pentane [13]. This suggests that it is possible to control the ET coupling strength between a pair of active reaction centers not only by structural modification but also by the chemical nature of the spacer element, as also noted by others [25–29].

### 3.3. Dependence of $V_{AB}$ on the orientation of the end groups of the molecules

In order to investigate the effect of the relative orientation of the end groups on ET, we calculated  $V_{AB}$  as a function of the angle,  $\phi$ , between the planes of the two terminal –CH<sub>2</sub> groups. Calculations were performed on structures obtained by rotating one of the –CH<sub>2</sub> groups in steps of 10° about the C(cage)–CH<sub>2</sub> bond while keeping the rest of the molecule fixed. The calculated variation of  $V_{AB}$  with the twist angle ( $\phi$ ) is shown in Fig. 2 and can be represented by a simple *cosine* function of  $\phi$ . It is clear that the value of  $V_{AB}$  is maximal when the two –CH<sub>2</sub> groups attached to the carborane cage are coplanar and is minimal when they are perpendicular to each other. This conformation dependent, through-bond electron tunneling between the donor and acceptor groups can be explained in terms of the super-exchange model. In the planar orientation of the two end groups, a strong coupling between the p-orbitals of the –CH<sub>2</sub> end groups and the vertex C-atoms of the cage is inherent. The orbitals of the vertex C-atoms subsequently couple to the cage-centered MO providing a pathway for the electron tunneling. This indirect interaction, in which the electron transfer between two reaction centers is mediated by intermediate bonds, is generally referred to as super-exchange interaction. For the perpendicular relative orientation of the two –CH<sub>2</sub> groups, the coupling between the p-orbitals of the –CH<sub>2</sub> end groups and the vertex C-atoms of the cage vanishes, breaking the super-exchange pathway for electron tunneling, thereby yielding a nearly vanishing value for  $V_{AB}$ . As proposed in a previous study [13,16], and also observed experimentally [32], the conformational dependence of ET offers an effective intrinsic mechanism for the control of electron transport in molecular systems – a property that can be of immense value in developing molecular-scale electronics.

Table 2

The ET coupling element ( $V_{AB}$ ) calculated with the Marcus–Hush *two-state* model for the 10- and 12-vertex carborane molecules

Molecule	Basis set	$V_{AB}^a$ (kJ/mol)	$V_{AB}^b$ (kJ/mol)
C <sub>4</sub> B <sub>8</sub> H <sub>12</sub> <sup>+</sup>	STO-3G	48.3	48.3
	DZP	52.6	53.7
C <sub>4</sub> B <sub>10</sub> H <sub>14</sub> <sup>+</sup>	STO-3G	37.6	37.5
	DZP	46.7	46.7

<sup>a</sup>  $V_{AB}$  calculated using the asymmetric (localized) geometry of the molecule.

<sup>b</sup>  $V_{AB}$  calculated using the symmetric (average) geometry of the molecule.

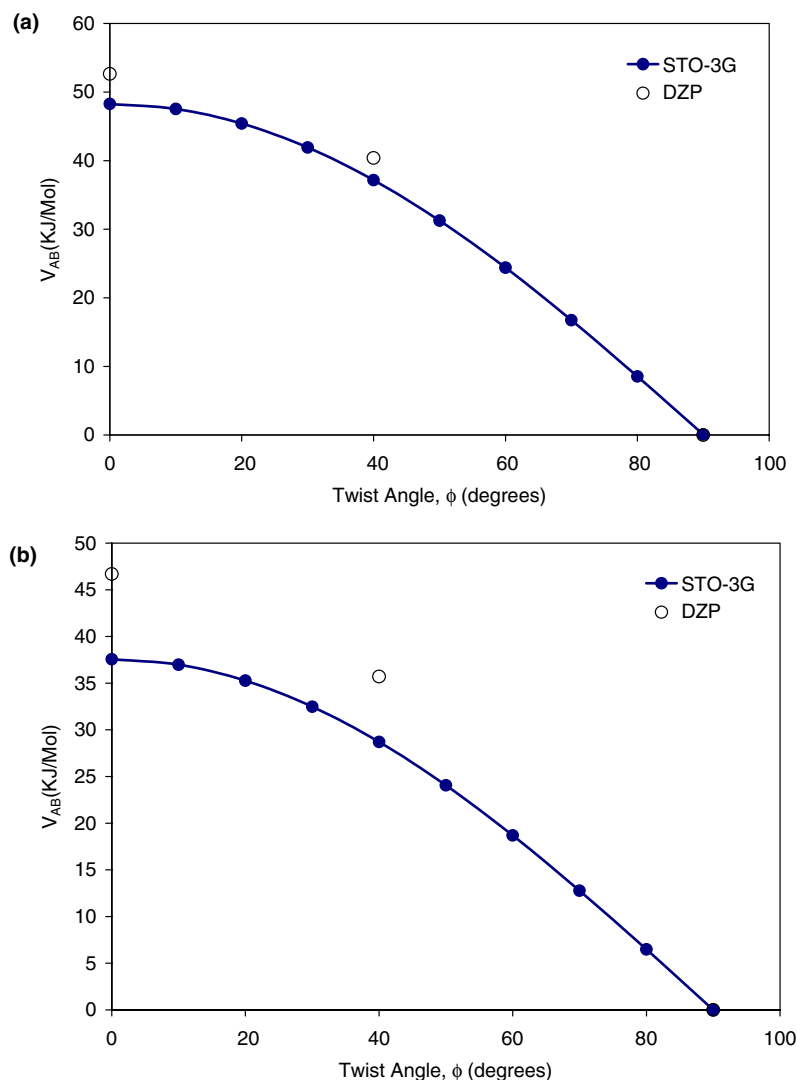


Fig. 2. The variation of the ET coupling element ( $|V_{AB}|$ ) as a function of twist-angle ( $\phi$ ) in (a) 10- and (b) 12-vertex carborane molecules using STO-3G and DZP basis sets.

#### 4. Conclusion

Ab initio electronic structure calculations have been performed to obtain the equilibrium structure and  $V_{AB}$  of  $-\text{CH}_2$  derivatized 10-vertex and 12-vertex carborane molecules. The value of  $V_{AB}$  is calculated to be larger by more than 35% in the KT approach than in the MH *two-state* model. The strength of the calculated ET coupling between the two active reaction centers is found to be only weakly dependent on the nuclear configuration of the carboranes considered here.

The switching characteristics with respect to rotation of the  $\pi$ -end groups can be simply described in terms of the *cosine* dependence on the twist angle between the terminal moieties, as also predicted for carbon cage systems [13]. The perpendicular orientation of the two  $\pi$ -end groups yields a nearly vanishing value of  $V_{AB}$ , while the parallel orientation gives the maximum value

for  $V_{AB}$ . Any other orientation between  $\pi$ -end groups leads to a finite orbital overlap and a finite ET coupling between the two reaction centers. The conformational dependence of ET, also observed in our previous studies on carbon cage systems [13], offers an effective mechanism for developing molecular switches [16].

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